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POLAROGRAPHIC INVESTIGATION OF SLAGS

REPORT 2

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This article gives the polarograms of the oxides of tin, cerium, and copper dissolved in dilute sodium borosilicate. /337*

The stannic oxide and copper oxide were of the "Ch. D. A." brand, and cerium dioxide was prepared according to [1]. Cerium nitrate was placed in a porcelain vessel and heated to 200° until the nitric oxides were completely removed. Then the temperature was increased to 400° and maintained for two hours. The product obtained was a lemon yellow.

The research method and the preparations were described previously [2].

Stannic Oxide

An example of a SnO_2 polarogram is given in Figure 1, and experimental data are given in Table 1. The polarograms were recorded at 1000° and the sensitivity was S = 1/5000.

As may be seen from Table 1, the diffusion current was directly proportional to the stannic oxide concentration in the melt (constant $i_d/N \cdot 10^3$).

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*Numbers in the margin indicate pagination of original foreign text.

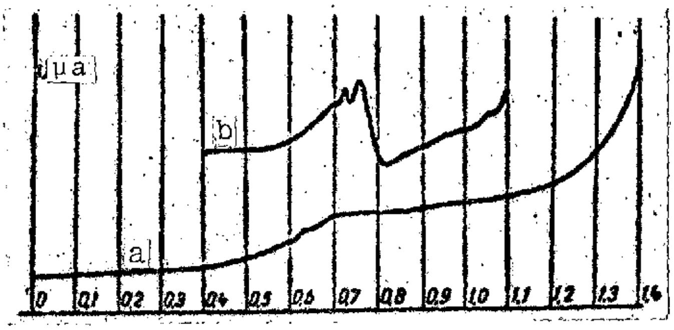

Figure 1. a- polarogram of stannic oxide; b- arbitrary polarogram of stannic oxide.

Graphs of the polarographic waves in the E, $\lg(i_d - i)$ coordinates greatly deviated from straight lines, more than the graphs in the E, $\lg(i/i_d - i)$ coordinates (Figure 2). Consequently, the polarograms are better described by the Geyrovskiy-Il'kovich equation than by the equation of concentration polarization.

There is a bend in the polarogram (Figure 1a). In order to explain this, arbitrary polarograms were recorded (Figure 1b), in which two peaks are clearly visible. It may be assumed that the reduction of tin on a microcathode takes place in two stages. /338

$$Sn^{4+} + 2e \rightarrow Sn^{2+},$$
$$Sn^{2+} + 2e \rightarrow Sn^{0}.$$

The values of the pre-logarithmic coefficients calculated from the experimental data are close to the values corresponding to n = 2. Apparently, the potentials for the reduction of Sn^{4+} to Sn^{2+} and of Sn^{2+} to Sn^{0} are close to each other, and the waves merge into one wave.

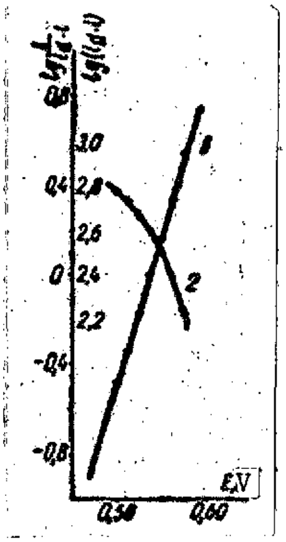

Figure 2. 1- Dependence of $\lg \frac{i}{i_d - i}$ on applied voltage for 0.00225 molar portions of SnO_2; 2- dependence of $\lg(i_d - i)$ on applied voltage for 0.002125 molar portions of SnO_2.

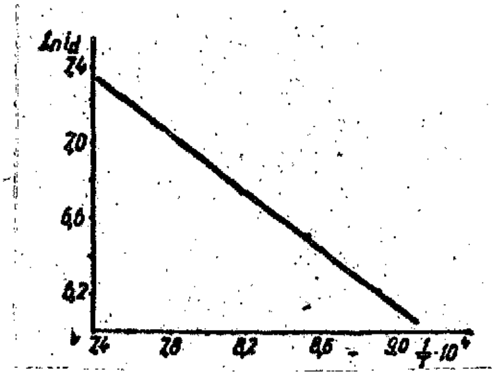

Figure 3. Temperature dependence of diffusion currents for 0.00596 molar portions of SnO_2.

The temperature dependence of the diffusion currents was determined for stannic oxide. The dependence of ln i_d on 1/T is shown in Figure 3. The points satisfactorily lie along a straight line, which points to the applicability of the equation

$$\ln i_d = A - \frac{B}{T}.$$

TABLE 1*

Molar portions N	Diffusion current i_d, μa	Halfwave potential $E_{1/2}$, V	$\frac{i_d}{N \cdot 10^5}$	$\frac{\Delta E}{\Delta \lg \frac{i}{i_d - i}}$
0,00255	475	0,550	186,3	0,107
0,00425	800	0,575	188,2	0,150
0,00596	1100	0,600	184,6	0,155
0,00766	1400	0,565	182,7	0,160

* Translator's Note: Commas in numbers indicate decimals.

Figure 4. Polarogram of cerium dioxide (0.001865 molar portions of CeO_2).

Cerium Dioxide

The cerium dioxide polarograms were recorded for seven concentrations from 0.000373 to 0.002608 molar portions of CeO_2. The attempt to produce a cathode wave was unsuccessful, but an anode wave was obtained. The polarogram /339 of cerium dioxide is shown in Figure 4, and the results of the experiments are given in Table 2. The polarograms were recorded with a sensitivity of S = 1/5000.

TABLE 2*

Molar portions N	Diffusion current i_d [μa]	Halfwave potential $E_{1/2}$, V	$\frac{i_d}{N \cdot 10^3}$	$\frac{\Delta E}{\Delta \lg \frac{i}{i_d - i}}$
0,000373	350	0,150	938,3	0,090
0,000746	700	0,160	938,3	0,125
0,000119	1050	0,180	938,3	0,128
0,001492	1375	0,185	921,6	0,135
0,001865	1700	0,175	911,5	0,165
0,002238	2075	0,175	927,1	0,170
0,002611	2400	0,195	919,1	0,170

* Translator's Note: Commas in numbers indicate decimals.

For cerium dioxide, just as for stannic oxide, constant $i_d/N \cdot 10^3$ is satisfactorily fulfilled.

The graphs of the polarographic waves in the E, $\lg(i/i_d - i)$ coordinates are straight lines, but it is impossible to reach any conclusion about the graphs in the coordinates E, and $\lg(i_d - i)$ (Figure 5). The pre-logarithmic coefficients are closer to the values for n = 2 than for n = 1 (theoretical values for n = 1 and n = 2 equal 0.256 and 0.128, respectively).

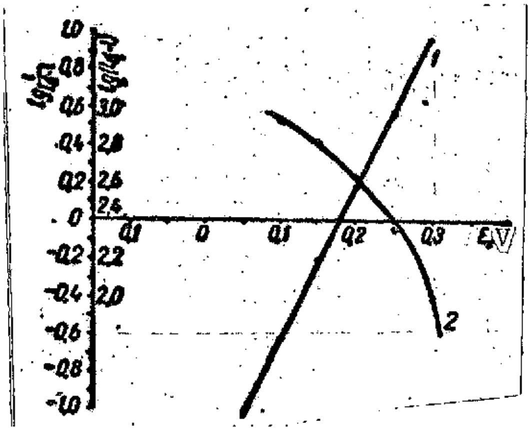

Figure 5. 1- dependence of $\lg \frac{i}{i_d - i}$ on applied voltage for 0.001119 molar portions of CeO_2; 2- dependence of $\lg(i_d - i)$ on applied voltage for 0.001119 molar portions of CeO_2.

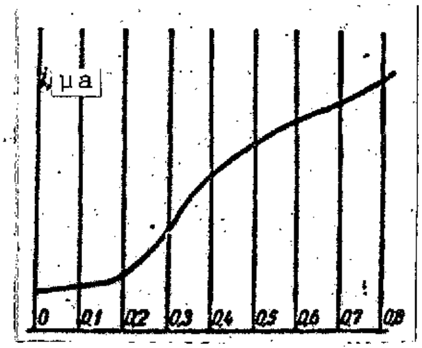

Figure 6. Polarogram of cuprous oxide (0.00322 molar portions of CuO).

How can the anode process be represented? It is known that cerium dioxide is thermally stable, and melts without decomposition at 2600° [3]. This means that there are no ions of lower valency in the melt. It may be assumed that oxidation takes place according to the following scheme on the microanode

$$Ce^{4+} - 2e = Ce^{6+}.$$

At higher concentrations, there is an increase in the pre-logarithmic coefficients. The temperature dependence of the diffusion currents was also found for cerium dioxide. A melt containing 0.001865 molar portions of CeO_2 was used. For cerium dioxide, the activation energy equalled 12.2 kcal/mole.

Cupric Oxide

The anode wave was recorded for cupric oxide. The cathode wave was indistinguishable. At high temperatures the oxide is unstable. At 1008°, the oxygen pressure above the cupric oxide reaches atmospheric pressure, due to the thermal dissociation of /340

CuO [5]. Apparently, in the melt CuO partially decomposes into Cu_2O and oxygen, and equilibrium occurs between CuO and Cu_2). The anode wave is formed due to oxidation of Cu_2O on the microcathode (Figure 6).

The waves were recorded at a sensitivity of S = 1/10000. The results of the experiments are given in Table 3. The waves are described by the Geyrovskiy-Il'kovich equation.

For cupric oxide, the activation energy equals 11.8 kcal/mole.

TABLE 3*

Molar portions N	Diffusion current i_d, μa	Halfwave potential $E_{1/2}$, V	$\frac{i_d}{N\cdot 10^3}$	$\frac{\Delta E}{\Delta \lg \frac{i}{i_d - i}}$
0,00161	1800	0,300	1118,0	0,115
0,00242	2700	0,305	1116,0	0,125
0,00322	3600	0,315	1118,0	0,135
0,00402	4500	0,335	1119,0	0,145

* Translator's Note: Commas in numbers indicate decimals.

Conclusions

The polarographic behavior was studied for the oxides of tin, cerium, and copper on a background of sodium borosilicate at 1000° using stationary platinum electrodes. It was established that there is a linear dependence between the diffusion current and the concentration of the oxide studied in the melt.

The oxide polarograms are better described by the Geyrovskiy-Il'kovich equation than by the Kol'tgof and Lingeyn equation. A gradual reduction is characteristic for stannic oxide. For cerium dioxide and cupric oxide, only anode waves were observed.

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16. Abstract

This article gives the polarograms of the oxides of tin, cerium, and copper dissolved in dilute sodium borosilicate. It was established that there is a linear dependence between the diffusion current and the concentration of the oxide in the melt.

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